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Review

The fate of DNAPL contaminants in non-consolidated subsurface systems – Discussion on the relevance of effective source zone geometries for plume propagation

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ABSTRACT

Dense non-aqueous phase liquids, i.e., DNAPLs and the evolving contaminant plumes in aquifers provide significant potential to pose hazards affecting both environment and human health. Therefore, a proper assessment of contaminant spreading within the subsurface is critical. This includes a sufficient characterization of governing parameters describing both the subsurface and the contaminant itself. Thereby, knowledge on the contaminant source zone and especially the source zone geometry, i.e., SZG is critically required, yet very uncertain. This study identifies current limitations and open research questions in the formation and shape determination of source zone geometry, as well as its relevance for contaminant plumes. Our literature review reveals that existing characterization methods are subject to data interpretation uncertainties, while the application of these methods on field scale is limited by technical demands and accompanied efforts. In a next step, methods to implement increased source zone information into calculation methods are discussed. By means of an exemplary application of selected assessment tools, i.e., plume response models, results clearly proof the relevance of SZGs for site assessment. However, existing plume response models consider over-simplified geometries that may compromise their suitability. Our findings identify the demand for improved characterization of complex SZGs and the need to better evaluate the dependency of DNAPL migration on system properties and external influences. With emphasized knowledge on the most relevant SZG features, the delineation of "effective" SZGs allowing for straightforward implementation into plume response models and an adaption of the latter to incorporate more information on SZGs should be possible.

1. Introduction

Contaminants that can be attributed to Dense Non-Aqueous Phase Liquids (DNAPLs) are among the major threats to subsurface ecosystems and resources (e.g., [1,2]). DNAPLs, as a compound group, can be divided into chlorinated solvents that are widely used for industrial processes such as dry-cleaning (e.g. [3–6],) and polycyclic aromatic hydrocarbon-dominated compounds. The latter ones, including coal tar and polychlorinated biphenyls, primarily emerge from wood burning and other sources of human activity (e.g. [7–9],). Such substances have been found to persist in groundwater bodies for several decades due to their low solubility in water as well as elevated resistance against (bio-) degradation [4,9–15]. Several DNAPL compounds are carcinogenic and mutagenic, posing significant risk to human health and other biota in the environment [16]. In addition, “the levels of contamination arising in evolving plumes are typically far above regulated drinking water standards” [5]. Besides being toxic themselves, DNAPL degradation often leads to the formation of daughter compounds such as vinyl chloride with even greater toxicological risks [6].

As dissolved contaminant plumes, often described by the steady-

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state maximum plume length L_{max}, may reach extents up to several kilometers (e.g., [17–19]; see also KORA reports[1]), adequate measures for hazard prevention are critically required. Here, successful site assessment generally supports decision making by selecting appropriate remediation techniques that have to be adapted to site-specific contamination scenarios [20–22]. Despite a large variety of remediation methods that have evolved during the last decades (for an overview, please refer to, e.g. [23–26],), there still remains a large number of sites affected by DNAPL contamination that are required to be properly assessed (e.g. [7,24,27,28],). In addition to plume remediation, it is possible to treat the source zone itself. However, source zone remediation in general is often unfeasible (e.g. [29–37],) and has been involved for a small portion of reported contaminated sites only [23]. DNAPL residuals require large hydraulic gradients to be remobilized (e.g. [38],) such that contaminations remain active contamination sources for several decades when treatment methods are not applied (e.g. [18,39],), but also under active treatment, especially for DNAPL residual saturations (e.g. [40–42],). Even if there are information on source location and distribution, an effective cleanup is still challenging (e.g., [15,21,22,24,31–37,43–49])

Since complete DNAPL mass removal is apparently not possible [27], partial source zone remediation has gained increasing interest (e.g. [50,51]). However, especially in comparison to plume remediation, this approach requires a more accurate quantification of factors that affect extensions of both source zone and plume (see section 2) and needs improved knowledge on the primary processes limiting source depletion, mass removal, and plume reduction at contaminated sites (e.g., [52]). Here, appropriate models (see Section 3) can help to support site assessment by simulating the spatiotemporal distribution of contaminants in highly complex DNAPL contamination scenarios including hydrogeological subsurface properties and variable hydraulic settings (see Fig. 1, and Section 2). These models assume simplified source zone geometries (SZGs) such as point sources, vertically or horizontally aligned line sources or, in very few cases, rectangles with different length-width aspect ratios. Such continuous geometries may rarely represent actual SZGs, which is largely due to the fact that the exact location of the source(s), their geometrical properties or both are commonly unknown (see Fig. 1; [10,53]). As several studies show that SZGs have major influence on plume propagation (e.g. [22,54–56],), its proper assessment and implementation into models can yield more reliable plume length estimations (see Table 1). This will also reduce uncertainties in assessment tools where model parameters, especially dispersivities [57,58], are usually varied during calibration (see Section 3.2).

This study combines insights and knowledge from existing literature, describing the formation and relevance of DNAPL contaminant sources and their geometry for plume propagation. First, the formation of SZGs is discussed. Second, measures for the field-scale characterization of SZGs are briefly introduced. This is followed by a discussion on approaches for plume response modeling. Finally, deficits and possibilities are reviewed in the context of current knowledge. Note that this study does not intend to provide a full review on DNAPL contamination scenarios (please refer to, among others, [2,17,19]), but rather a scientific discussion on the importance of SZG as a factor that is critical for plume extension and evolution in non-consolidated subsurface systems, but still underrated in existing approaches for estimating L_{max}.

2. DNAPL source zone formation in subsurface porous media and existing methods for source zone characterization

2.1. Source zone formation

A significant number of recent investigations suggest that SZGs at contaminated sites play a key role in down-gradient plume propagation (e.g., [34,46,49,51,54–56,59–67]). After their release, DNAPLs, having high interfacial tension with water, migrate through the subsurface in response to gravity and capillary forces [7] and are distributed to form a so-called "source zone" (e.g., [4,17,38,68]; see also Fig. 1, stage 1). The migration is highly irregular, as it is found to depend on DNAPL type (viscosity, density, interfacial tension with water; e.g., [69]) and aquifer properties including the distribution of both permeability and porosity within the sediment matrix (e.g. [38,51,64,70–72],). Processes controlling source zone formation are also affected by external stresses (e.g., seasonal hydrological variations such as precipitation or artificial influences such as water abstraction; e.g. [51,63],). Once the original DNAPL contamination release has ceased, the forces driving its movement decrease until eventually DNAPL phases within pore spaces become entrapped at areas of residual saturation as ganglia or blobs and are, therefore, disconnected (e.g. [19,53,69,73],). Especially in regions above deterministic heterogeneities with less hydraulic permeability (e.g., lenses or bedrock), so-called "pools" enable remarkable DNAPL volumes to become entrapped for long time (e.g. [10,17,74–78],). In such regions with relatively high DNAPL saturation, mass transfer to the aqueous phase occurs, leading to dissolved contaminant plumes in groundwater. These plumes are subject to site-specific aquifer properties and microbial activity (e.g. [19,60,62,79],).

2.2. Source zone characterization

To the best knowledge of the authors, the relevance of the previously stated impacts for source zone formation and, consequently, for L_{max} is not sufficiently clear yet. Indeed, being an essential requirement for remediation, a successful site evaluation, including the assessment of possible site-specific dissolved contaminant transport behavior, strongly depends on SZG characterization. Therefore, source zones should individually be considered in addition to conventional plume evaluations (e.g., [56,61,66,67,80]). Currently, a large number of geohydraulic, geochemical, geotechnical and geophysical methods for field-scale subsurface characterization, for advanced groundwater monitoring and, hence, for determining the previously listed factors controlling SZG formation exists (for a comprehensive overview, please refer to, e.g. [81,82],). To obtain missing hydrogeological information between observation wells (e.g., hydraulic conductivity field), for example, multi-level tracer tests can be used in combination with stochastic modeling [83]. Such field measurements, if carefully planned and properly accomplished, help to reduce the aforementioned uncertainties in parameter estimation and support the strategic use of plume response models (see section 3).

Most monitoring and exploration approaches are limited to sample aqueous DNAPL concentrations and are, therefore, suitable for determining plume distributions only. However, source zone characterization itself, i.e., sampling the DNAPL phase for field-scale determination of DNAPL distributions, bears much more demands and has rarely been done. First attempts show promising results for SZG characterization. The most straightforward approach is phase sampling within soils (e.g., [13,84–86]), including soil gas surveys such as the Radon method [87,88]. Some methods such as membrane interface probe (see Co. Geoprobe Systems[2]) or laser-induced fluorescence (see Co. Dakota Technologies[3]) are related to direct push [89]. Other methods can be applied by using existing groundwater observation wells. Examples for such methods are cross-well radar [90,91], vertical induction profiling [92], or partition inter-well tracer tests [93]. A third class of methods can be attributed to non-invasive on-site technologies

[1] www.natural-attenuation.de (last access 09/12/2018).

[2] https://geoprobe.com/mip-membrane-interface-probe (last access 08/20/2018).

[3] http://www.dakotatechnologies.com/learn-more/intro-to-lif/overview (last access 08/20/2018).

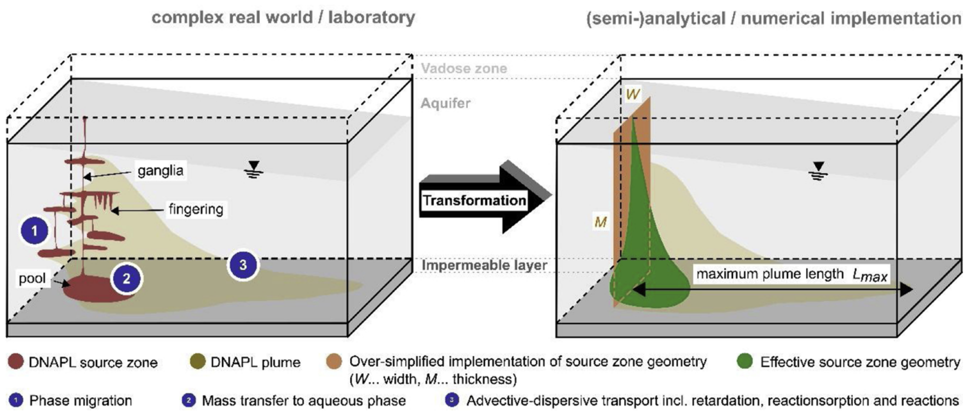

Fig. 1. Idealized concept of DNAPL contamination scenarios in non-consolidated subsurface porous media (*not to scale*). Shown are the spatial distribution of a hypothetical, real-world source zone (*red*) and its corresponding dissolved contaminant plume (*ochre*). In addition, the three stages of DNAPL contamination scenarios are depicted (*blue*). SZG is represented as complex (*red* on *left side*) and as frequently over-simplified (*orange plane* on *right side*; with width *W* and thickness *M*) for calculating steady-state maximum plume length L_{max} (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 1
Values for steady-state maximum plume lengths L_{max} (rounded to whole meters) and relative change of L_{max} in comparison to base case (factors in parentheses), obtained by applying the plume length estimation tool NAFLA [117]. In a fourth scenario, values for L_{max} are calculated utilizing the analytical model after [55]. Input data is according to [117], see Table 2. Results show that L_{max} is very sensitive to SZG width and height, while values depend on the model being selected.

SZG type implemented in model after reference number	1-D horizontal line source in 2-D domain [107]	1-D vertical line source in 2-D domain [54]	2-D horizontal line source in 2-D domain [108]	2-D planar source in 3-D domain [55]
Base case (using data from [117])	8	85	3790	61
Increasing height of source by factor of 4	8 (-)	1358 (16 x)	3790 (-)	355 (5.8 x)
Increasing width of source by factor of 4	131 (16 x)	85 (-)	60,642 (16 x)	85 (1.4 x)

(for an overview, please also refer to [94]), as for instance ground-penetrating radar [95–97], electrical resistivity/impedance and self-potential tomography [98–100], magnetic resonance imaging [66], or spectrally induced polarization [101].

Up to now, several drawbacks limit the feasibility of the aforementioned SZG characterization methods at contaminated sites. By phase sampling within soils, DNAPL saturations can directly be determined. However, interpolation between sampling locations appears insufficient, so that detailed SZG characterization requires a large number of samples. The majority of the other methods provide only qualitative results for DNAPL distributions. Also, detection quality strongly depends on subsurface properties, arising large uncertainties in the typically non-homogeneous domains, including false positives and negatives. Highly complex DNAPL mass distributions require a large number of subsurface samples to reduce uncertainties particularly for the characterization of SZGs (e.g., [25]). Therefore, technical and also financial limitations substantially limit the wide application of source zone characterization methods. Although the aforementioned characterization methods provide highly valuable insights into subsurface systems and the spatial distributions of contaminants, they should be supported by (semi-)analytical and numerical simulations in order to forecast the maximum space being potentially affected by dissolved DNAPL contamination. Specifically, relations between impacts (measureable system properties such as hydraulic gradient), corresponding SZGs (which are estimated via SZG characterization methods as presented above) and dissolved contaminant plume extents (see Section 3.2) should be identified. Together with an enhanced understanding of DNAPL contamination evolution (see Fig. 1), these relations might then be usable for delineation of more generalized methods that would further improve the assessment and remediation of the large number of sites being affected by DNAPL contamination.

3. Simulation approaches utilized for site assessment

3.1. Models for simulating DNAPL contamination scenarios

In general, existing simulation models related to DNAPL contamination scenarios (see Fig. 1) can be differentiated into three categories (see Fig. 1; please also refer to [102] for a comprehensive overview on simulation models) covering the respective different stages of DNAPL contamination scenarios that partially overlap in time (see Fig. 1 and section 2). Beginning with stage 1, the DNAPL release and phase migration through the (un-)saturated zone leads to the source zone formation (e.g., [19]). This first stage can be described by physics-based multiphase flow models (e.g. [15,74],). Stage 2 represents the mass transfer to the aqueous phase; a large number of research have been conducted in the field of dissolution models (e.g. [41,64,65,73,103–106],). Stage 3 is represented by so-called plume response models that cover the advective-dispersive contaminant transport down-stream from the source under consideration of retardation, reactions and degradation. The latter models are typically either (semi-)analytical (e.g. [54,55,107–111],) or numerical models (e.g. [62,112],). Plume response models have been applied for site pre-assessment (e.g. [18,113,114],), but suffer from large uncertainties that are discussed in the following.

3.2. Plume response models for estimating dissolved contaminant spreading

Plume response models allow for initial site assessment by estimating dissolved contaminant spreading and can also be utilized for the quantification of flow and transport parameters in case of measured values for plume length. The most straightforward plume response models are relatively simple closed-form algebraic expressions that approximate actual field conditions in making assumptions such as homogeneous domain, uniform flow velocity, fully water-saturated porous medium and spatially constant dispersivities (e.g., [18]). Furthermore, these models (e.g. [54,55],) implement straightforward reaction mechanisms, posing particular limitations for DNAPL substances that are typically subject to sequential reaction chains with transformation from the original substance to simple hydrocarbons that become vulnerable to final decay using electron acceptors such as oxygen, nitrate or sulfate (e.g. [17,115–117],). Here, more complex (semi-)analytical models that involve such reaction chains have evolved during the last three decades (e.g. [118–121],). Ultimately, numerical reactive transport models (e.g. [62,112],) are capable to simulate highly complex field conditions such as different scales of aquifer heterogeneities

Table 2
Input data for calculations in Table 1, after [117].

Parameter (a, b, c, and d indicate whether used by [107,54,108,55], respectively)	Value
Electron donor molar mass ($g\,mol^{-1}$) [a,b,d]	84.349
Electron donor concentration ($mg\,L^{-1}$) [a,b,c,d]	246
Stoichiometric factor electron acceptor/electron donor (-) [a,b,c,d]	4.159
Electron acceptor molar mass ($g\,mol^{-1}$) [a,b,d]	96.056
Electron acceptor concentration ($mg\,L^{-1}$) [a,b,c,d]	364.5
Transverse vertical dispersivity (m) [a,d]	0.05
Transverse horizontal dispersivity (m) [b,c,d]	0.5
Aquifer thickness (m) [a,d]	2.5
Porosity (-) [b, c]	0.16
Source width (m) [b,c,d]	14
Characteristic concentration in reaction zone ($mg\,L^{-1}$) [c]	0.001

or multicomponent mass transfer interactions.

Apart from the previously listed assumptions, plume response models typically assume simplified SZGs (e.g., thickness M times width W in the calculation method after [55]; see Fig. 1). By using the modeling tool NAFLA [117], steady-state maximum plume lengths $L_{\max}$ have been calculated for exemplary contamination scenarios with a fully penetrating source under consideration of the closed-form equations after [54,107,108] and with defined parameters (see Table 2). Results clearly proof that, compared to other model parameters, values for $L_{\max}$ strongly depend on the definition of source thickness or area, respectively (see Table 1). A major influence can also be attributed to the transversal dispersivity that controls the mixing between two reactants within the plume, as revealed by other studies as well (e.g., [107,109]). However, quantification of this parameter at field scale is difficult (e.g. [57,122,123],), if not more complicated and challenging than characterizing SZGs. As seasonal external stresses such as recharge through precipitation, fluctuating groundwater levels and other impacts may change SZG over time, existing plume response models with over-simplified, fully-penetrating SZGs may not provide accurate estimates for $L_{\max}$. Up to now, only few works [18,113,114] have evaluated plume length estimations by comparing field data with and model results. Together with the previously stated assumptions, the applicability of plume response models for site assessment has yet to be proven. To overcome the over-simplification of SZGs, partially penetrating sources, i.e., discontinuous DNAPL source zones should be further investigated [18]. Here, the relevance of geometrical source properties should be examined, in particular the length, area, or alignment of regions with elevated DNAPL saturation, i.e., DNAPL sub-zones that lead to dissolution. Furthermore, approaches how to transfer complex to effective SZGs should be identified. First attempts could demonstrate the sensitivity of DNAPL sub-zones for mass transfer [41]. However, up to now, the subsequent impact of on $L_{\max}$ has yet not been sufficiently carried out.

4. Discussion and outlook

4.1. Recent trends and general controversies

Due to temporal, technical and financial limitations for high-resolution investigations on field scale (see Section 2), it is a common practice to approximate processes of contaminant spreading in porous media. Consequently, plume response models implement over-simplified representations of real-world SZGs based on best characterization available, hence, leading to specific levels of uncertainty (see Section 3). Here, a compromise between efforts to increase complexity and acceptance of uncertainty has to be found.

Likewise, a number of studies has focused on processes occurring at source zones, where source properties were investigated through 2-D/3-D experimental or modeling works on laboratory scale for quantifying processes leading to mass depletion and to determine the contamination longevity when no remediation is applied (e.g., [14,22,34,35,38,44,53,56,71,73,124,125]). Source depletion is found to be largely dependent on SZG, DNAPL dissolution properties and hydrodynamic subsurface characteristics (e.g. [45,56,61,65,66,71,73,126,127]).

Furthermore, the quantitative characterization of DNAPL mass transfer to the aqueous phase has received much attention including the introduction of descriptive parameters such as the ganglia-to-pool ratio (GTP ratio; e.g., [63]), where pools and ganglia are differentiated via quantification of DNAPL saturation (for more details, please refer to, e.g. [73,87,128],). GTP ratio relates to contaminant mass distribution and is dependent on geological and hydrodynamic subsurface properties (e.g. [73],). Multiple studies (e.g. [73,106,104],) found that most mass transfer models (see Section 3.1) are closely related to GTP ratio. Therefore, models are capable to describe the process of mass dissolution properly and are partially verified against experimental results. However, a transfer to field scale has yet to be proven.

4.2. Concept of "effective" source zone geometries

While the aforementioned approaches concisely describe important processes being active at the source zone that will change its geometry, they do not allow for quantification of SZG for a specific problem in the field. Real-world SZGs are expected to consist of highly irregular shapes, including multiple centers of mass and locations of formation (see Fig. 1). Few studies have been conducted to improve the understanding in source zone formation, indicating that assuming over-simplified geometries may not be appropriate for adequate estimations of contaminant plumes (e.g., laboratory analyses by [53,72]). Considering the limitations in hydrogeological exploration, the exhaustive knowledge on processes at source zones as well as the apparent dependency of contaminant plumes on SZG dimensions (see Table 1 and Fig. 1) and on other factors, we suggest that future research should increase its attention on the description of field-site influences that govern the formation and distribution of SZGs.

In this context, the transformation of complex, real-world SZGs to "effective" SZGs would allow for a more straightforward prediction of contaminant plume evolution when extended information about the source zone is missing due to insufficient field-scale source zone characterization (see Section 3.2 and Fig. 1). These effective SZGs, intended to condense complex information to a practicable level, are derived from or characterized by subsurface and DNAPL properties as well as external stresses. With this gained knowledge, the linkage between source mass removal and associated contaminant concentrations in groundwater may become better characterized. Of course, uncertainties arising from the still existing information loss during the transformation from complex to effective SZGs have to be quantified by appropriate evaluation procedures (e.g., by continuous source zone and plume monitoring at field sites). However, these uncertainties are expected to be much smaller than the ones arising from employing over-simplified SZGs.

4.3. Conclusions

Research works provide the critically needed scientific background for the development of robust assessment tools that are required for complex problems such as contaminated site management and, therefore, they have wide social and economic implications. Such assessment tools are required to evaluate potential site management strategies, quantify associated risks to the environment and human health. For reliable predictions, these tools should therefore be:

(i) based on or verified by experimental results on laboratory and field scale,
(ii) applicable to sites that are undergoing external stresses, hydrogeological, or hydrogeochemical factors, and

(iii) as simple as possible, but as complex as required such that they are usable in practice for a large number of existing sites.

Acknowledging these requirements for assessment tools and based on the literature review on the present state of research, we postulate that the most important challenges for a robust prediction of L_{max} (or steady-state plume extensions) and, consequently, the respective remediation techniques can be summarized as the following ones.

(i) Stronger attention should be spent on the involvement of source zone geometries for L_{max} estimation: By enhancing knowledge on SZGs, i.e., through application of models that are capable to simulate SZG formation (e.g., [73]), and incorporating this information into L_{max} predictions, i.e., through adaptable plume response models (see section 3), we hypothesize that such improved involvement of SZGs will yield better estimations of L_{max}.
(ii) SZGs need to be characterized and correlated to the individual geohydraulic conditions: A combination of laboratory, field-site and numerical experiments should be employed to gather information on source zone formation and its characterization based on the respective aquifer properties (e.g., layering), DNAPL type (e.g., viscosity) and external stresses (e.g., groundwater recharge).
(iii) We require easily adaptable and transferable descriptions of "effective source geometries" that can be derived from site characteristics: We understand that a key challenge will be the formulation and derivation of a transfer approach that is able to determine the spatially distributed mass at the source zone that is dependent upon aquifer and DNAPL properties as well as external stresses. Due to several complexities (porous media, hydrodynamics, and scale), an "effective source geometry" will resolve into a better plume length description based on an appropriate source zone characterization (see Fig. 1).

Overall, our exemplary modeling scenarios clearly show a major relevance of SZGs for plume propagation. Our literature review suggests that there have been few attempts to find best-representative, site-specific "effective" SZGs. We consider this as the currently most critical knowledge gap that restricts our ability to adequately predict L_{max} and ease evaluation of contaminant spreading and assessment within the frame of current limitations of monitoring and exploration.

Conflict of interest

The authors declare no conflict of interest. The funders had no role in the design of the study, in the collection, analyses or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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